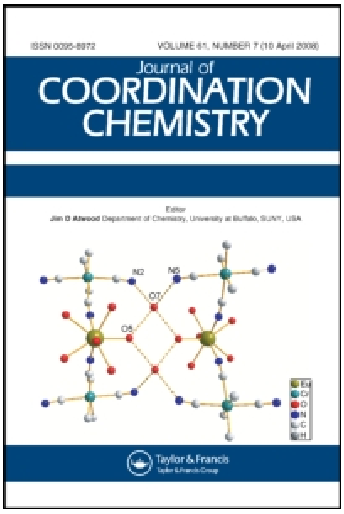

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

SYNTHESIS OF ONE-AND TWO-DIMENSIONAL ZINC AND CADMIUM COMPLEXES WITH 4, 4'-BIPY

L. Pan[a]; N. W. Zheng[a]; Y. G. Wu[a]; X. L. Jin[b]; X. Y. Huang[c]
[a] Department of Chemistry, University of Science & Technology of China, Hefei, Anhui, P. R. China [b] Department of Chemistry, Peking University, Beijing, P. R. China [c] Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian, P. R. China

To cite this Article Pan, L. , Zheng, N. W. , Wu, Y. G. , Jin, X. L. and Huang, X. Y.(1999) 'SYNTHESIS OF ONE-AND TWO-DIMENSIONAL ZINC AND CADMIUM COMPLEXES WITH 4, 4'-BIPY', Journal of Coordination Chemistry, 47: 2, 269 — 277

To link to this Article: DOI: 10.1080/00958979908023059

URL: http://dx.doi.org/10.1080/00958979908023059

J. Coord. Chem., 1999, Vol. 47, pp. 269–277
Reprints available directly from the publisher
Photocopying permitted by license only

SYNTHESIS OF ONE- AND TWO-DIMENSIONAL ZINC AND CADMIUM COMPLEXES WITH 4,4′-BIPY

L. PAN[a], N.W. ZHENG[a,*], Y.G. WU[a], X.L. JIN[b] and X.Y. HUANG[c]

[a]*Department of Chemistry, University of Science & Technology of China, Hefei, Anhui 230026, P.R. China;* [b]*Department of Chemistry, Peking University, Beijing 100871, P.R. China;* [c]*Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, P.R. China*

(Received 16 April 1998)

The zinc(II) and cadmium(II) complexes $[Zn(4,4'\text{-bipy})(SCN)_2]_\infty$ **1** and $[Cd(4,4'\text{-bipy})\text{-}(SCN)_2]_n$ **2** have been synthesized and their crystal structures determined by X-ray crystallography. Complex **1** is monoclinic, space group C2/c, with $a = 18.076(5)$, $b = 5.190(1)$, $c = 17.315(4)$ Å; $\beta = 115.54(2)$, $V = 1465.8(8)$ Å^3, calculated density 1.530 g cm^{-3}, $Z = 4$. In this compound, the rod-like ligand 4,4′-bipy bridges Zn(II) centres, and the NCS groups are terminally coordinated. (N–Zn–N) is 108.5°, resulting in the formation of a zigzag Zn–bipy–Zn chain. These chains are arranged in parallel fashion. The 4,4′-bipy ligands of adjacent layers are separated by 3.95 (Å). Complex **2** is monoclinic, space group C2/c, $a = 11.902(2)$, $b = 11.745(2)$, $c = 10.500(2)$ Å; $\beta = 109.71(3)$, $V = 1381.8(4)$ Å^3, calculated density 1.849 g cm^{-3}, $Z = 4$. In this structure, the cadmium(II) ion is slightly distorted octahedral and the SCN groups act as doubly bridging ligands connecting cadmium atoms to form zigzag chains, separated by 4,4′-bipy to create two-dimensional planes.

Keywords: Zinc; cadmium; pseudohalides; 4,4′-bipy; X-ray structures

INTRODUCTION

There has been considerable interest in zeolitic properties such as stability and open framework structures based on coordination chemistry, due to accompanying catalytic and ion-exchange properties.[1,3] The rational design and construction of microporous materials from molecular building units is a great challenge. 4,4′-Bipy as a linear exodentate ligand has been

---

[*] Corresponding author.

coordinated to metals to obtain a number of one-,[4] two-[5] and three-dimensional[6] extended solids. Cadmium adopts various geometries and coordination numbers from four to eight,[7,8] suitable for constructing various structures. A number of systematic structures based on Cd with halides were studied.[9] Thiocyanate binds metal ions as a bridge to form a chain structure[10] in many compounds when the sulfur atom coordinates to the metal ion. Therefore, combining the Cd(II) ion with SCN^- and 4,4′-bipy was attempted. A novel structure, which possesses zigzag cadmium ion and thiocyanate chains separated by 4,4′-bipy to form an infinite neutral two-dimensional structure, was synthesized. By the same synthetic methods, we find that zinc(II) only coordinates with the nitrogen atom of thiocyanate to form a neutral infinite one-dimensional chain.

EXPERIMENTAL

Physical Measurements

Elemental analyses were performed on a Perkin-Elmer 2400 instrument. Thermogravimetric analysis (TGA) was carried out using a Rigaku instrument under Ar, the heating rate being 10°C min^{-1}. X-ray powder data were recorded at a scanning rate of 0.05° s^{-1}, using a Rigaku Dmax γ_A X-ray diffractometer with graphite monochromatized CuKα radiation (λ=1.54178 Å).

Preparation and Crystal Data

Compound **1** was obtained by reacting an aqueous mixture containing $ZnSO_4 \cdot 7H_2O$ (0.547 g, 2 mmol) and KSCN (0.3887 g, 4 mmol) with an ethanol solution (1 : 2 v/v) of 4,4′-bipy $\cdot$ $2H_2O$ (0.3844 g, 2 mmol). The resulting product was collected after a few minutes at room temperature as a white microcrystalline material. The solid was washed with ethanol ($3 \times 10\,cm^3$) and ether ($3 \times 10\,cm^3$), and dried under vacuum for 24 h to give 0.48 g of solid (71.1%). *Anal.* (%) found: C, 43.01; H, 2.38; N, 16.63. Calcd. for Zn(4,4′-bipy)$(SCN)_2$: C, 42.64; H, 2.37; N, 16.58. A single crystal suitable for X-ray analysis was obtained by diffusing an aqueous solution of mixed by $ZnSO_4$ (0.10 M) and KSCN (0.20 M) through ethylene glycol ($3\,cm^3$) into an ethanol solution of 4,4′-bipy (0.1 M). After a few days, colourless plates had collected at the ethanol/ethylene glycol interface. The same complex was also obtained using hydrothermal synthesis. A mixture of $ZnSO_4$, 4,4′-bipyridine and KSCN was sealed in a Teflon lined stainless steel autoclave and heated at 160°C for 24 h under autogeneous pressure. The clear colourless crystals were collected and was identified by comparison *via* powder X-ray diffraction.

Crystal data for compound **1**: $C_{12}H_8N_4S_2Zn$, $M = 337.72$, monoclinic, space group C2/c, $a = 18.076(5)$, $b = 5.190(1)$, $c = 17.315(4)$ Å, $\beta = 115.54(2)°$, $V = 1465.7(8)(7)$ Å^3, $Z = 4$, $D_c = 1.530\ \mathrm{g\,cm^{-3}}$, $F(000) = 680$, $\mu = 19.79\ \mathrm{cm^{-1}}$. Data collection ($0 \leq 2\theta \leq 50°$) was performed at 296 K on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated MoKα radiation ($\lambda = 0.71073$ Å). Cell parameters were obtained by a least-squares fit to the setting of 25 well-centred reflections with $18.32 \leq 2\theta \leq 25.3°$. A total of 1491 reflections was measured with the variable-speed ω-scan technique, of which 920 unique data were observed with $I \geq 2\sigma(I)$ and these were used in the structure solution and refinement; $R = 0.063$, $R_w = 0.073$.

Compound **2** was obtained by the addition of an aqueous solution (20 cm^3) of $CdSO_4 \cdot \frac{8}{3}H_2O$ (1.026 g, 4 mmol) and of KSCN (0.777 g, 8 mmol) to an ethanol solution (30 ml) of 4,4′-bipy · $2H_2O$ (0.77 g, 4 mmol). The resulting product was collected after a few minutes as a colourless microcrystalline material. This solid was washed with water (3 × 20 cm^3) and ethanol (3 × 20 cm^3) and dried under vaccum for 24 h to give 0.53 g of product (34.6%). A single crystal suitable for X-ray analysis was obtained by diffusing an ethanol solution of 4,4′-bipy (0.1 M) through 4 cm^3 of a mixture of water and ethanol (1 : 1) as a buffer zone into an other aqueous solution of $CdSO_4$ (0.1 M) and KSCN (0.2 M). Some weeks later, white crystal prisms and rhombs were collected from the mixed water and ethanol solution.

Crystal data for compound **2**: $C_{12}H_8N_4S_2Cd$, $M = 384.74$, monoclinic, space group C2/c, $a = 11.902(2)$, $b = 11.745(2)$, $c = 10.500(2)$ Å, $\beta = 109.71(3)°$, $V = 1381.8(4)$ Å^3, $Z = 4$, $D_c = 1.849\ \mathrm{g\,cm^{-3}}$, $F(000) = 752$, $\mu = 18.72\ \mathrm{cm^{-1}}$. Data collection ($5.02 \leq 2\theta \leq 50°$) was performed at 293 K on a Rigaku AFC6S diffractometer using graphite-monochromized MoKα radiation ($\lambda = 0.71073$ Å). Cell parameters were obtained by a least-squares fit to the setting of 25 well-centred reflections with $10 \leq 2\theta \leq 24°$. A total of 1212 reflections was measured with the variable-speed ω-scan technique, of which 1064 unique data were observed with $I \geq 2\sigma(I)$ and were used in the structure solution and refinement; $R = 0.0305$, $R_w = 0.0727$. The data were corrected for absorption (empirical, based on ψ scan).[11] The two structures were solved by direct methods and refined on F by full-matrix; least-squares techniques using programs in SHELXTL-97 package. Final refinement cycles were performed by full-matrix least-squares with anisotropic thermal parameters for all non-hydrogen atoms and assigned isotropic thermal parameters for hydrogen atoms. Full lists of crystallographic data are available from the authors upon request.

RESULTS AND DISCUSSION

Thermogravimetric Analyses

Complex **1** (3.98 mg) was heated to 600°C in argon. The TGA displayed a weight loss corresponding to one 4,4′-bipy (found 57.8% calcd. 57.0%) in the temperature range 370–410°C. Weight loss continued above 500°C. Complex **2** was heated to 560°C in argon. In the range 320–360°C, weight change corresponding to the loss of one 4,4′-bipy as well as the decomposition of two thiocyanate ions (found 57.3%, calcd. 57.8%) was observed. Final products of pyrolysis were ZnS (wurtzite) (complex **1**) and hexagonal CdS (complex **2**) containing a little cubic CdS, identified by X-ray powder diffraction. XRD traces showed that the ZnS and CdS were nanocrystalline with average particle sizes being 60 nm and 30 nm, respectively.

Structures

Final coordinates for non-hydrogen atoms of **1** and **2** are listed in Table I and important bond lengths and angles are given in Table II. In complex **1** (Figure 1), the Zn(II) ion is coordinated through four nitrogen atoms from two 4,4′-bipy ligands and two NCS groups. The average N–Zn–N angle of 109.38° is close to ideal tetrahedral. The Zn–N(4,4′-bipy) bond lengths (2.032 Å) are slightly short as compared to $[Zn(4,4'\text{-bipy})_2(H_2O)_2]SiF_6$ (2.158 Å)[12] and $[Zn(4,4'\text{-bipy})_2]SiF_6$ (2.157 Å).[13]

A chain structure for the complex is shown in Figure 2. As can been seen, 4,4′-bipy bridges Zn(II) centres, and the NCS groups are terminal. The metal–metal distance, separated by 4,4′-bipy, is 11.1 Å. The angle of Zn(II) with 4,4′-bipy (N–Zn–N) is 108.5°, resulting in the formation of a zigzag Zn–bipy–Zn chain, every Zn(II) site repeated by 18.08 Å. Two pyridine rings of each 4,4′-bipy unit are coplanar, as was seen earlier.[5,12]

There is disorder associated with the SCN anion; the sulphur atom is disordered atom, though the nitrogen and carbon atoms are well-ordered (see Table II). 4,4′-Bipy ligands of two adjacent layers are separated by 3.95 Å and arranged in parallel fashion. This may mean that there is a very weak π–π interaction between layers.

TABLE I Final atomic cooordinates and standard deviations (in parentheses) for the non-hydrogen atoms

	x/a	*y/b*	*z/c*	*B(eq)*
Complex **1**				
Zn	0.5000	0.1711(2)	0.2500	4.29(5)
S(1A)	0.7439(5)	0.6306(17)	0.3512(6)	11.8(5)
S(1B)	0.7535(13)	0.522(4)	0.4004(14)	13(1)
N(1)	0.5000(4)	−0.0576(10)	0.3453(3)	3.8(2)
N(2)	0.6030(5)	0.3457(16)	0.2951(5)	6.6(3)
C(1)	0.4311(5)	−0.1289(17)	0.3469(6)	6.1(4)
C(2)	0.4293(5)	−0.3101(18)	0.4058(6)	6.6(4)
C(3)	0.4999(4)	−0.4079(12)	0.4682(4)	3.4(2)
C(4)	0.5710(4)	−0.3274(17)	0.4654(5)	5.4(3)
C(5)	0.5691(5)	−0.1464(16)	0.4046(5)	5.2(3)
C(6)	0.6636(6)	0.448(2)	0.3238(7)	7.3(5)
Complex **2**				
Cd(1)	0.5000	0.58176(3)	0.7500	0.0259(2)
S(1)	0.29427(11)	0.58037(11)	0.53084(13)	0.0400(3)
N(1)	0.3810(4)	0.5781(3)	0.8869(4)	0.0347(9)
N(2)	0.5000	0.7792(4)	0.7500	0.0280(11)
N(3)	0.5000	1.3804(4)	0.7500	0.0297(11)
C(1)	0.3455(4)	0.4868(4)	0.4474(4)	0.0293(10)
C(2)	0.4464(4)	0.8386(4)	0.8209(5)	0.0347(10)
C(3)	0.4428(4)	0.9561(4)	0.8227(4)	0.0310(10)
C(4)	0.5000	1.0170(5)	0.7500	0.0258(13)
C(5)	0.5000	1.1432(5)	0.7500	0.0282(13)
C(6)	0.6005(4)	1.2052(4)	0.7538(5)	0.0362(11)
C(7)	0.5978(4)	1.3211(4)	0.7548(5)	0.0340(11)

TABLE II Selected bond lengths (Å) and angles (°) for the two compounds

Complex **1**			
Zn–N(2)	1.908(8)	N(1)–C(5)	1.312(9)
Zn–N(2)i	1.909(8)	N(2)–C(6)	1.12(1)
Zn–N(1)i	2.032(5)	C(1)–C(2)	1.40(1)
Zn–N(1)	2.033(5)	C(2)–C(3)	1.37(1)
S(1A)–C(6)	1.63(1)	C(3)–C(4)	1.37(1)
S(1B)–C(6)	1.64(2)	C(3)–C(3)ii	1.46(1)
N(1)–C(1)	1.310(9)	C(4)–C(5)	1.40(1)
N(2)i–Zn–N(2)	123.3(5)	N(1)–C(1)–C(2)	121.8(7)
N(2)i–Zn–N(1)	105.5(3)	C(3)–C(2)–C(1)	121.2(7)
N(2)–Zn–N(1)	106.7(3)	C(2)–C(3)–C(4)	115.4(6)
N(2)i–Zn–N(1)i	106.7(3)	C(2)–C(3)–C(3)ii	122.5(8)
N(2)–Zn–N(1)i	105.6(3)	C(4)–C(3)–C(3)ii	122.0(8)
N(1)i–Zn–N(1)	108.5(3)	C(3)–C(4)–C(5)	120.7(7)
C(1)–N(1)–C(5)	118.4(6)	N(1)–C(5)–C(4)	122.1(7)
C(1)–N(1)–Zn	121.0(5)	N(2)–C(6)–S(1A)	170(1)
C(5)–N(1)–Zn	120.5(5)	N(2)–C(6)–S(1B)	155(1)
C(6)–N(2)–Zn	178.1(9)		
Complex **2**			
Cd(1)–N(2)	2.319(5)	N(2)–C(2)	1.330(5)
Cd(1)–N(1)	2.333(4)	N(2)–C(2)a	1.330(5)
Cd(1)–N(1)a	2.333(4)	C(2)–C(3)	1.381(6)

TABLE II (*Continued*)

Cd(1)–N(3)b	2.365(5)	C(3)–C(4)	1.382(5)
Cd(1)–S(1)a	2.7369(16)	C(4)–C(3)a	1.382(5)
Cd(1)–S(1)	2.7369(16)	C(4)–C(5)	1.482(8)
S(1)–C(1)	1.645(5)	N(1)–C(1)c	1.160(6)
N(2)–Cd(1)–N(1)	91.05(9)	N(1)a–Cd(1)–S(1)	92.22(11)
N(2)–Cd(1)–N(1)a	91.05(9)	N(3)b–Cd(1)–S(1)	89.66(3)
N(1)–Cd(1)–N(1)a	177.90(19)	S(1)a–Cd(1)–S(1)	179.32(6)
N(2)–Cd(1)–N(3)b	180.000(1)	C(1)–S(1)–Cd(1)	93.69(16)
N(1)–Cd(1)–N(3)b	88.95(9)	C(1)c–N(1)–Cd(1)	139.3(3)
N(1)a–Cd(1)–N(3)b	88.95(9)	C(2)–N(2)–Cd(1)	121.7(3)
N(2)–Cd(1)–S(1)a	90.34(3)	N(1)e–C(1)–S(1)	179.0(4)
N(1)–Cd(1)–S(1)a	92.22(11)	N(2)–C(2)–C(3)	123.7(4)
N(1)a–Cd(1)–S(1)a	87.77(11)	C(2)–C(3)–C(4)	119.1(4)
N(3)b–Cd(1)–S(1)a	89.66(3)	C(3)a–C(4)–C(3)	117.6(5)
N(2)–Cd(1)–S(1)	90.34(3)	C(3)a–C(4)–C(5)	121.2(3)
N(1)–Cd(1)–S(1)	87.77(11)		

Symmetry operations are (i): $1-x, y, \frac{1}{2}-z$; (ii): $1-x, -1-y, 1-z$; (a): $1-x, y, \frac{3}{2}-z$; (b): $x, y-1, z$; (c): $x, 1-y, 1+z$; (d): $x, y+1, z$; (e): $x, 1-y, z-\frac{1}{2}$.

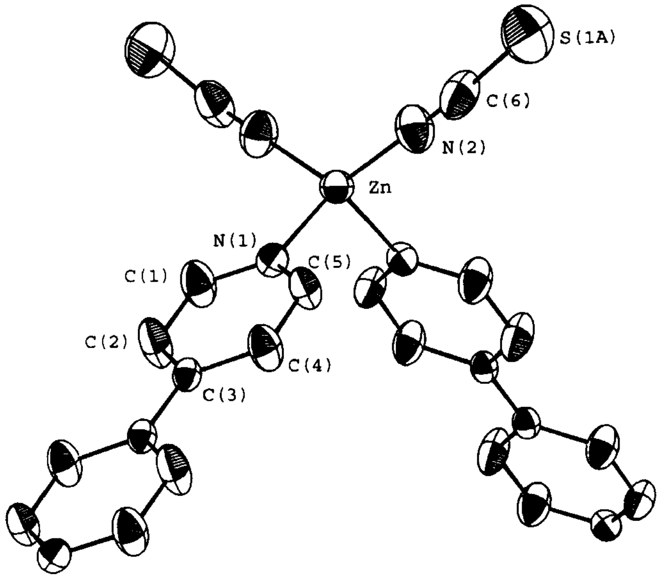

FIGURE 1 The basic building block of the zinc compound with hydrogen atoms omitted for clarity.

Although the distance between face to face pyridine rings is somewhat larger than the layer separation in graphite (3.35 Å), the weak interaction may play an important role in the self-assembly of the structure. Therefore, further studies of this kind of crystal structure using other metals and ligands in order to increase the π–π interaction between the planes are under way.

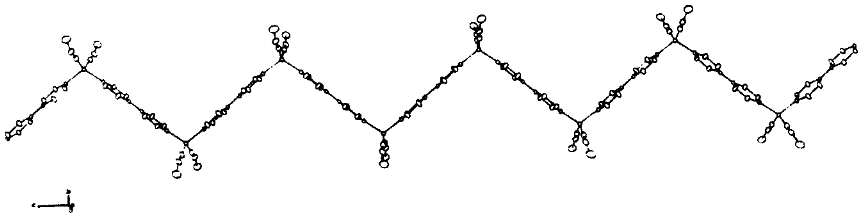

FIGURE 2 Structure of the chain arrangement in the zinc compound.

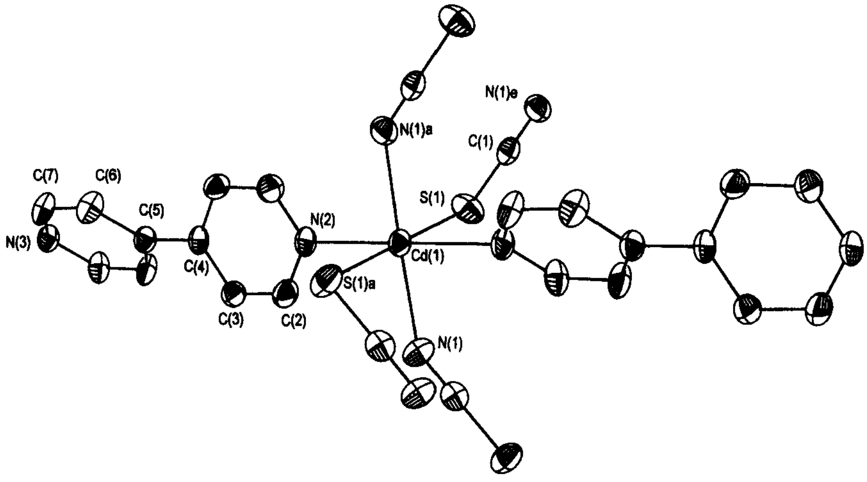

FIGURE 3 A perspective view of $[Cd(4,4'\text{-bipy})(SCN)_2]_n$. Hydrogen atoms are omitted for clarity.

For complex **2**, the coordination of the cadmium centre is shown in Figure 3. Each cadmium, which is slightly distorted octahedral, is coordinated by two nitrogen atoms from SCN^- and two nitrogen atoms from 4,4′-bipy as complex **1** and also by two sulphur atoms from SCN^- anions. The CdN_4S_2 unit comprises an equatorial plane which defined by the four nitrogen atoms and two apical positions occupied by sulphur. There is clearly elongated octahedral distorsions with Cd(1)–S(1) = 2.7369(16) Å, Cd(1)–S(1)a = 2.7369(16) Å, Cd(1)–N(1) = 2.333(4) Å, Cd(1)–N(1)a = 2.333(4) Å, Cd(1)–N(2) = 2.319(5) Å and Cd(1)–N(3)b = 2.365(5) Å. As shown in the Figure 4, the crystal structure of $Cd(4,4'\text{-bipy})(SCN)_2$ reveals that the 4,4′-bipy ligands bridge metal ions to form straight chains extended along one direction. The other direction has doubly bridged parallel SCN^- ions connecting the metal centres to form zigzag with Cd ··· Cd distances of 5.59 Å and Cd ··· Cd ··· Cd angles 139.8°. The unit cell is illustrated in Figure 5; two kinds of chains cross to construct the two dimensional plane

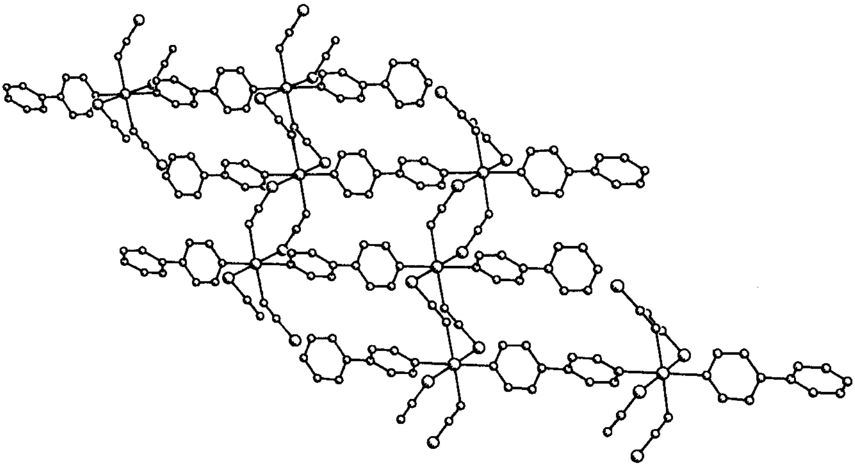

FIGURE 4 Extended structure of the cadmium compound.

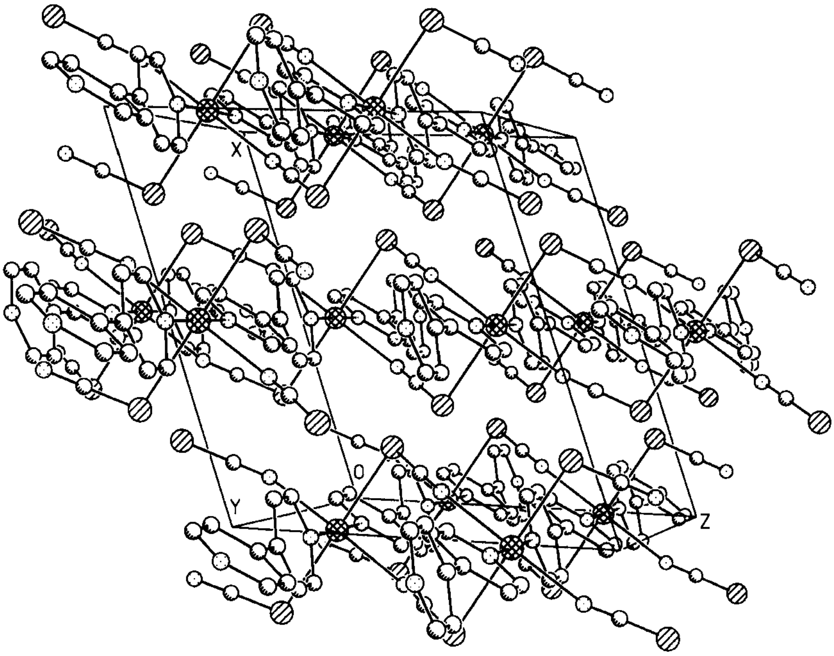

FIGURE 5 A sketch of the unit cell contents of the cadmium complex.

structure along the *a* axis. Adjacent planes are interconnected by van der Waals forces. The dihedral angle of the two pyridine rings of 4,4′-bipy is 39.9° and the approximate maximum size of pores in the structure is 5.6 × 11.8 Å.

An infinite anionic $[Cd(SCN)_3^-]_\infty$ polymeric zigzag chain has been found in cadmium complexes,[14] in which Cd(II) is bridged by three SCN^- anions to form unique chains with an extended π-conjugation system within a polymeric $-[M-S-C\equiv N]-M$ structure and high polarizability. In the present compound, there is no high delocalization of SCN^- ions.

Acknowledgments

This work was supported by the Anhui Provincial Foundation of Natural Science Research and the National Nature Science Foundation of China.

References

[1] M. Fujita, Y.J. Kwon, S. Washizu and K. Ogura, *J. Am. Chem. Soc.* **116**, 1151 (1994).
[2] J. Kim, D. Whang, J.I. Lee and K. Kim, *J. Chem. Soc., Chem. Commun.* 1400 (1993).
[3] O.M. Yaghi, G. Li and H. Li, *Nature* 703 (1995).
[4] B.F. Abrahams, B.F. Hoskins and G. Winter, *Aust. J. Chem.* **43**, 1759 (1990).
[5] J. Lu, T. Paliwala, S.C. Lim, C. Yu, T. Niu and J. Jacobson, *Inorg. Chem.* **36**, 923 (1997).
[6] O.M. Yaghi and H. Li, *J.* Am. Chem. Soc. **117**, 10401 (1995). R.W. Gable, B.F. Hoskin and R. Robson, *J. Chem. Soc., Chem. Commun.* 1677 (1990).
[7] D.G. Tuck, *Rev. Inorg. Chem.* **1**, 209 (1979).
[8] C.K. Schauer and O.P. Anderson, *J. Chem. Soc.* **109**, 3646 (1987).
[9] M. Neiuwenhuyzen, W.T. Robinson and C.J. Wilkins, *Polyhedron*, **10**, 211 (1991).
[10] H. Zhang, X. Wang, H. Zhu, W. Xiao and B.K. Teo, *J. Chem. Soc.* **119**, 5463 (1997).
[11] P. Coppens, L. Leiserowitz and D. Robinocich, *Acta Cryst.* **18**, 1035 (1965).
[12] R.W. Gable, B.F. Hoskins and P. Robson, *J. Chem. Soc., Chem. Commun.* 1667 (1990).
[13] S. Subramanian and M.J. Zaworotko, *Angew. Chem. Int. Ed. Engl.* **34**, 2127 (1995).
[14] H. Zhang, X. Wang and B.K. Teo, *J. Am. Chem. Soc.* **118**, 11813 (1996).